(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号
特開2003－13200
（P2003－13200A）
(43)公開日　平成15年１月15日(2003.1.15)

(51)Int.Cl.⁷	識別記号	FI	テーマコード(参考)
C23C 14/06		C23C 14/06	B 4G046
C01B 31/02	101	C01B 31/02	101Z 4K029
C23C 14/32		C23C 14/32	F 4K030
16/26		16/26	
16/50		16/50	

審査請求　未請求　請求項の数６　ＯＬ　（全７頁）

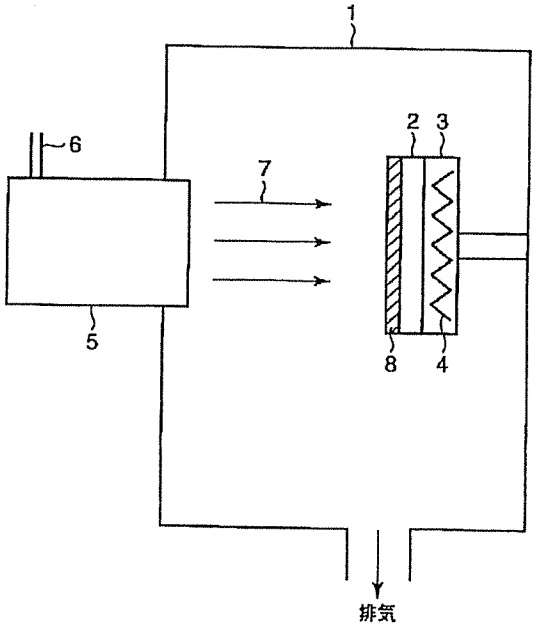
(21)出願番号　特願2001－199056(P2001－199056)
(22)出願日　平成13年６月29日(2001.6.29)

(71)出願人　000006208
三菱重工業株式会社
東京都千代田区丸の内二丁目５番１号
(72)発明者　山下　信樹
神奈川県横浜市金沢区幸浦一丁目８番地１
三菱重工業株式会社基盤技術研究所内
(72)発明者　園部　裕之
長崎県長崎市深堀町五丁目717番１号　三菱重工業株式会社長崎研究所内
(74)代理人　100058479
弁理士　鈴江　武彦　（外４名）

最終頁に続く

(54)【発明の名称】　硬質炭素膜およびその製造方法

(57)【要約】　（修正有）
【課題】　空気中での潤滑性を向上させ、さらに耐熱性を向上させた硬質炭素膜を提供する。
【解決手段】　半導体もしくは金属を０．１～３０原子％含むアモルファス構造の炭素膜からなることを特徴とする。半導体もしくは金属は、シリコン、アルミニウム、クロムもしくはチタンのいずれかよりなる。成膜方法には、イオンビーム蒸着法またはプラズマ蒸着法を用いる。



PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-013200

(43)Date of publication of application : 15.01.2003

(51)Int.Cl. C23C 14/06

C01B 31/02

C23C 14/32

C23C 16/26

C23C 16/50

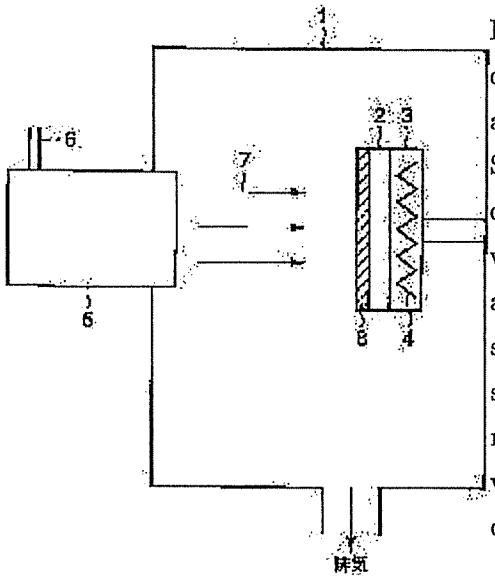
(21)Application number : 2001-199056

(22)Date of filing : 29.06.2001

(71)Applicant : MITSUBISHI HEAVY IND LTD

(72)Inventor : YAMASHITA NOBUKI
SONOBE HIROYUKI
WATANABE TOSHIYA

(54) HARD CARBON FILM AND MANUFACTURING METHOD THEREFOR



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hard carbon film with improved lubricity in the air and improved heat resistance.

SOLUTION: This hard carbon film is characterized in that it consists of a carbon film which includes a semiconductor or metal 0.1-30 atom% and having an amorphous structure. The semiconductor or the metal consists of any of silicon, aluminum, chromium and titanium. The method for forming the film uses an ion-beam vapor deposition method or a plasma vapor deposition method.

CLAIMS

[Claim(s)]

[Claim 1]A hard carbon film consisting of a carbon film of amorphous structure 0.1-30 atom % Containing a semiconductor or metal.

[Claim 2]The hard carbon film according to claim 1, wherein said semiconductor or metal consists of silicon, aluminum, chromium, or the titanium.

[Claim 3](a) Mixed gas with an organic compound containing hydrocarbon, a semiconductor, or metal, (b) Mixed gas of an organic compound and oxygen containing hydrocarbon, a semiconductor, or metal, Or a manufacturing method of a hard carbon film covering a hard carbon film with an ion-beam-deposition method which generates ion of mixed gas with an organic compound containing (c) hydrocarbon, a semiconductor or metal, and oxygen, and accelerates this ion, and with which a substrate is irradiated.

[Claim 4]A manufacturing method of the hard carbon film according to claim 3 setting accelerating voltage of said ion as 50-2000V.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a hard carbon film and manufacturing methods for the same to the member of which abrasion resistance is required, such as slide members, information-machines-and-equipment memory storage, etc., such as a bearing of various rotary machines, and a slide.

[0002]

[Description of the Prior Art]A hard carbon film is a rigid film called i-carbon film in which research began to be started from the second half of the 1970s. This hard carbon film has an amorphous-like integrated state as which the crystallinity of short period is regarded by the integrated state of a carbon atom.

[0003]As a formation method of said hard carbon film, plasma chemistry vapor phase growth which is indicated by JP,64-31974,A, for example is known.

[0004]The physical properties of a hard carbon film are 30GPa order and high hardness in Vickers hardness, and since they have the character excellent in abrasion resistance, lubricity, insulation, chemical resistance, etc., they are applied to coating to a tool, several kinds of machinery moving part, and electronic parts.

[0005]

[Problem(s) to be Solved by the Invention]However, although the hard carbon film obtained with the conventional method has a coefficient of friction as low as 0.1 or less in a vacuum and a nitrogen gas atmosphere and being excelled in the friction characteristic, in the air, it is reported that a coefficient of friction increases and lubricity falls. Especially the hard carbon film obtained with the conventional method is weak with heat, if it is heated, it will change to soft graphite membrane, and also if an elevated temperature is used, it will burn and it will disappear. For this reason, service temperature is restricted with 300 ** or less, and there was an inapplicable problem in the tool used in a severe environment, and several kinds of machinery moving part.

[0006]It is going to provide a hard carbon film where this invention raised the lubricity in the inside of the air and which raised heat resistance further, and a manufacturing method for the same.

[0007]

[Means for Solving the Problem]0.1-30 atom % A hard carbon film concerning this invention is characterized for a semiconductor or metal by consisting of a carbon film of amorphous structure to include.

[0008]. According to this invention, the crystallinity of short period is looked at by integrated state of a carbon atom. By making a carbon film which has an amorphous-like integrated state contain a semiconductor or metal (preferably silicon, aluminum, chromium, or the titanium) of a specific amount, a hard carbon film which raised lubricity in inside of the air and raised heat resistance further can be obtained.

[0009]Mixed gas with an organic compound in which a manufacturing method of a hard carbon film concerning this invention contains (a) hydrocarbon, a semiconductor, or metal, (b) Mixed gas of an organic compound and oxygen containing hydrocarbon, a semiconductor, or metal, Or a hard carbon film is covered with an ion-beam-deposition method which generates ion of mixed gas with an organic compound containing (c) hydrocarbon, a semiconductor or metal, and oxygen, and accelerates this ion and with which a substrate is irradiated.

[0010]In a manufacturing method of a hard carbon film concerning this invention, it is preferred to set accelerating voltage of said ion as 50-2000V.

[0011]According to this invention method, a hard carbon film which raised lubricity in inside of the air and raised heat resistance further can be manufactured.

[0012]Mixed gas with an organic compound in which a manufacturing method of another hard carbon film concerning this invention contains (a) hydrocarbon, a semiconductor, or metal, (b) Mixed gas of an organic compound and oxygen containing

hydrocarbon, a semiconductor, or metal, Or plasma of mixed gas with an organic compound containing (c) hydrocarbon, a semiconductor or metal, and oxygen is generated, and negative pulse voltage is impressed to a substrate put into this plasma.

[0013]In a manufacturing method of another hard carbon film concerning this invention, it is preferred that pulse voltage impressed to said substrate shall be -10 kV from -1kV.

[0014]According to the option of this invention, a hard carbon film which raised lubricity in inside of the air and raised heat resistance further can be manufactured.

[0015]

[Embodiment of the Invention]Hereafter, the hard carbon film concerning this invention is explained.

[0016]This hard carbon film consists of a carbon film of the amorphous structure 0.1-30 atom % Containing a semiconductor or metal.

[0017]As for said semiconductor or metal, it is preferred that it is silicon, aluminum, chromium, or the titanium.

[0018]If content of said semiconductor or metal is made into less than 0.1 atom %, it will become difficult to obtain the hard carbon film which has a coefficient of friction in the inside of the atmosphere and the performance for which heat resistance exceeds elegance conventionally. On the other hand, if the content of said semiconductor or metal exceeds 30 atom %, the hard carbon film which has an integrated state of the shape of amorphous [as which the crystallinity of short period is regarded by the integrated state of a carbon atom], It becomes a mixture of black lead, silicon, a semiconductor like aluminum, or metal, and becomes an elasticity film of 5 or less GPa of Vickers hardness, and there is a possibility that the original outstanding character of a hard carbon film may be spoiled.

[0019]Next, the manufacturing method of the hard carbon film concerning this invention is explained in detail with reference to drawing 1.

[0020]Drawing 1 is a schematic diagram showing the device for manufacturing the hard carbon film concerning this invention.

[0021]Evacuation of the vacuum housing 1 is carried out by the evacuation device which is not illustrated. The holder 3 for holding the substrate 2 which should be processed is formed in said vacuum housing 1. The heating heater 4 connected to the power supply and thermoregulator which are not illustrated is built in said holder 3. Said holder 3 may establish a rolling mechanism if needed.

[0022]The ion source 5 is attached so that said vacuum housing 1 may be countered with said holder 3. It accelerates and this ion source 5 irradiates said holder 3 with that ion as the ion beam 7 while generating the ion of the mixed gas which was introduced

from the gas introducing pipe 6 and which is mentioned later. The Kauffmann type ion source, a bucket type ion source, etc. are applied, for example from the point of the homogeneity of membraneous quality, and productivity in said ion source 5.

[0023]A hard carbon film is manufactured by the following methods.

[0024]First, the substrate 2 is attached to the holder 3 and evacuation of the vacuum housing 1 is carried out to a predetermined degree of vacuum. It continues and said substrate 1 is heated to desired temperature with the heating heater 4 built in said holder 2.

[0025]Subsequently, mixed gas with the organic compound containing (a) hydrocarbon, a semiconductor, or metal, (b) The mixed gas of the organic compound and oxygen containing hydrocarbon, a semiconductor, or metal, Or mixed gas with the organic compound containing (c) hydrocarbon, a semiconductor or metal, and oxygen is introduced into the ion source 5 (for example, Kauffmann ion source) through the gas introducing pipe 6, and said vacuum housing 1 is controlled to a predetermined degree of vacuum. The ion source 5 is operated in this state, said substrate 2 is irradiated with the ion beam 7, and the hard carbon film 8 of amorphous structure is formed.

[0026]The machine member etc. as which the abrasion resistance which consists of stainless steel, tool steel, bearing steel, cemented carbide, etc., for example is required as said substrate can be mentioned.

[0027]As for the cooking temperature of said substrate, it is preferred to use 30-200 **.

[0028]Benzene is especially preferred although what is necessary is just to use the hydrocarbon which can introduce methane, ethane, acetylene, benzene, etc. as a gas easily, for example as hydrocarbon in the mixed gas introduced into said ion source 5.

[0029]In the organic compound containing said semiconductor or metal, it is preferred that it is silicon, aluminum, chromium, or the titanium as said semiconductor or metal.

[0030]As an organic compound containing the semiconductor or metal in the mixed gas introduced into said ion source 5, For example, hetero methyl disiloxane $(CH_3)_4Si$, Triethylaluminum $(C_2H_5)_3$aluminum, Bis(cyclopentadienyl) clo NIUMU $(C_5H_5)_2Cr$ and cyclopentadienyl cyclo OKUTATETORAENII titanium (C_5H_5) (C_8H_8) Ti can be used.

[0031]As an organic compound containing the semiconductor or metal, and oxygen in the mixed gas introduced into said ion source 5, For example, tetramethylsilane $(CH_3)_6Si_2O$, Tris(acetylacetonate) aluminum $(C_5H_7O_2)_3$aluminum, Tris (acetylacetonate) clo NIUMU $(C_5H_7O_2)_3Cr$, tetraethoxy titanium $(OC_2H_5)_4Ti$, etc. can be used.

[0032]As for the ion acceleration voltage in said ion source 5, it is preferred to use 50-2000V. When ion acceleration voltage is made into less than [50V], a possibility that a lot of hydrogen may mix, may become polymer-like, and may serve as an elasticity

film is in a film. When ion acceleration voltage exceeds 2000V, there is a possibility that a membranous self-sputtering effect may become strong and membrane formation speed may become low extremely. More desirable ion acceleration voltage is 100-1000V.

[0033]Next, the manufacturing method of another hard carbon film concerning this invention is explained in detail with reference to drawing 2.

[0034]Drawing 2 is a schematic diagram of another film deposition system for manufacturing the hard carbon film concerning this invention.

[0035]Evacuation of the vacuum housing 11 is carried out by the evacuation device which is not illustrated. The holder 13 which installs the substrate 12 which is a processing member is connected to the bias power supply 15 which can impress negative pulse voltage via the high insulation feed through 14. The plasma 16 is generated in said vacuum housing 11. This plasma 16 introduces the mixed gas mentioned later in said vacuum housing 11 from the gas introducing pipe 17, And microwave is introduced into the vacuum housing 11 via the waveguide 18 from the microwave power supply 19, It is made to generate by forming the magnetic field which absorbs most efficiently said microwave introduced near [substrate 12] said with the magnet coils 20a and 20b of the couple which countered said vacuum housing 11 mutually, respectively, and has been arranged.

[0036]Various plasma sources, such as high frequency plasma, the Helicon plasma, inductively coupled plasma, may be used in addition to generating of the plasma by such a structure.

[0037]A hard carbon film is manufactured by the following methods.

[0038]First, the substrate 12 is installed in the holder 13 and evacuation of the vacuum housing 11 is carried out to a predetermined degree of vacuum. (a) Mixed gas with the organic compound containing hydrocarbon, a semiconductor, or metal, (b) Introduce mixed gas with the organic compound containing the mixed gas of the organic compound and oxygen containing hydrocarbon, a semiconductor, or metal, (c) hydrocarbon and a semiconductor or metal, and oxygen in said vacuum housing 11 through the gas introducing pipe 17, and set it as a desired pressure. In the part of the request in said vacuum housing 11, an absorbable magnetic field is efficiently formed for microwave by sending desired current through the magnet coils 20a and 20b of a couple. The plasma 16 is generated by introducing the microwave of a desired output in said vacuum housing 11 via the waveguide 18 in this state from the microwave power supply 19.

[0039]Simultaneously with said plasma generation, desired pulse voltage is impressed to said substrate 12 from the bias power supply 15 via the high insulation feed through

14.

[0040]The hard carbon film 21 is formed on said substrate 12 surface by the above process.

[0041]The machine member etc. as which the abrasion resistance which consists of stainless steel, tool steel, bearing steel, cemented carbide, etc., for example is required as said substrate can be mentioned.

[0042]Benzene is especially preferred although what is necessary is just to use the hydrocarbon which can introduce methane, ethane, acetylene, benzene, etc. as a gas easily, for example as hydrocarbon in the mixed gas introduced into said vacuum housing 11.

[0043]In the organic compound containing said semiconductor or metal, it is preferred that it is silicon, aluminum, chromium, or the titanium as said semiconductor or metal.

[0044]As an organic compound containing the semiconductor or metal in the mixed gas introduced into said vacuum housing 11, For example, hetero methyl disiloxane $(CH_3)_4Si$, Triethylaluminum $(C_2H_5)_3$aluminum, Bis(cyclopentadienyl) clo NIUMU $(C_5H_5)_2Cr$ and cyclopentadienyl cyclo OKUTATETORAENII titanium (C_5H_5) (C_8H_8) Ti can be used.

[0045]As an organic compound containing the semiconductor or metal, and oxygen in the mixed gas introduced into said vacuum housing 11, For example, tetramethylsilane $(CH_3)_6Si_2O$, Tris (acetylacetonate) clo NIUMU $(C_5H_7O_2)_3Cr$, tetraethoxy titanium $(OC_2H_5)_4Ti$, etc. can be used.

[0046]As for the pulse voltage impressed to said substrate, being referred to as -1kV--10kV is preferred. When pulse voltage impressed to this substrate is made into less than [-1kV], there is a possibility of a lot of hydrogen mixing into a film, becoming polymer-like, and becoming an elasticity film. On the other hand, when the pulse voltage impressed to said substrate exceeds -10kV, there is a possibility that a membranous self-sputtering effect may become strong and membrane formation speed may become low extremely.

[0047]

[Example]Hereafter, with reference to drawing 1 and drawing 2 which mentioned the desirable example above, it explains in detail.

[0048](Examples 1-3 and comparative example 1) The substrate 2 which becomes the holder 3 from high speed tool steel (JIS:SKH55) was attached first, and evacuation of the inside of the vacuum housing 1 was carried out to below $1.5x10^{-3}$Pa.

[0049]Subsequently, material gas was supplied from the gas introducing pipe 6 of the Kauffmann ion source 5. As hydrocarbon said material gas Benzene (C_6H_6), As an organic compound containing silicon, hetero methyl disiloxane $(CH_3)_4Si$, As an organic

compound containing oxygen (O_2), silicon, and oxygen, tetramethylsilane $(CH_3)_6Si_2O$, The ion source 5 was supplied from the gas introducing pipe 6 with the gestalt the mixed gas shown in the following table 1, or benzene independent (comparative example 1), using triethylaluminum $(C_2H_5)_3$aluminum as an organic compound containing aluminum. In Example 1, as introductory gas, namely, benzene, hetero methyl disiloxane, In Example 3, benzene was used [Example 2] as introductory gas by the comparative example 1 using the mixed gas of oxygen, using the mixed gas of benzene and triethylaluminum as introductory gas, using the mixed gas of benzene and a tetramethylsilane as introductory gas. It mixed by the setting-up flow rate shown in the following table 1 with the flow control device which is not illustrated, and each gas controlled the flow, and supplied it from the gas introducing pipe 6. At this time, said vacuum housing 1 was controlled to $7x10^{-1}$Pa.

[0050]The ion source 5 was operated in such the state, it irradiated with the ion beam 7 on the substrate 2 by the ion acceleration voltage 500V and ion current density 1 mA/cm^2, and the 1-micrometer-thick hard carbon film 8 was formed.

[0051]

[Table 1]

[0052]About the carbon film obtained by Examples 1-3 and the comparative example 1, it investigated by Raman-spectrum analysis. As a result, any carbon film showed the large peak near 1500-1600-cm^{-1}, and has checked that it was a hard carbon film of amorphous structure.

[0053]About the carbon film obtained by Examples 1-3 and the comparative example 1, X linear-light electronic spectroscopic analysis analyzed elementary composition, and Vickers hardness was measured. The coefficient of friction of said carbon film was counted with the ball one disk type frictional testing machine. As conditions for a rubbing test, 2N and speed were carried out in 0.1 m /, and atmosphere was a stainless steel (JIS:SUS304) ball and load the temperature of 30 **, and 400 ** for the mating material sec. The result is shown in the following table 2.

[0054]

[Table 2]

[0055]The hard carbon film of Examples 1 and 2 which have the amorphous structure containing silicon so that clearly from the result of said table 2, And it turns out that the hard carbon film of Example 3 which has the amorphous structure containing aluminum shows the low coefficient of friction of a single or less figure by the rubbing test in the atmosphere with a temperature of 30 ** compared with the hard carbon film of the comparative example 1. Especially the point that should be noted is a point which shows the coefficient of friction with a low hard carbon film of Examples 1-3 also in the rubbing test in the atmosphere with a temperature of 400 **. It damages at this temperature and the hard carbon film of the comparative example 1 shows a high friction coefficient. This shows that heat resistance of the hard carbon film of Examples 1-3 is improving substantially.

[0056]The organic compound gas which contains chromium in Examples 1-3 mentioned above as an organic compound containing a semiconductor or metal (for example, bis(cyclopentadienyl) clo NIUMU; $(C_5H_5)_2Cr$), The organic compound gas containing titanium (for example, cyclopentadienyl cyclo OKUTATETORAENII titanium; $(C_5H_5)(C_8H_8)Ti$), The organic compound gas which contains chromium as an organic compound containing a semiconductor or metal, and oxygen (for example, tris (acetylacetonate) clo NIUMU; $(C_5H_7O_2)_3Cr$), Even if it used the organic compound gas (for example, tetraethoxy titanium; $(OC_2H_5)_4Ti$) containing titanium, the hard carbon film which has performance equivalent to Examples 1-3 was able to manufacture.

[0057](Examples 4-6 and comparative example 2) The substrate 12 which becomes the holder 13 from high speed tool steel (JIS:SKH55) was attached first, and evacuation of the inside of the vacuum housing 1 was carried out to below $1x10^{-3}$Pa. It continued, material gas was introduced in said vacuum housing 11 through the gas introducing

pipe 17, and it controlled to 5x10 $^{-2}$Pa. As hydrocarbon said material gas Benzene (C_6H_6), As an organic compound containing silicon, hetero methyl disiloxane $(CH_3)_4Si$, As an organic compound containing oxygen (O_2), silicon, and oxygen, tetramethylsilane $(CH_3)_6Si_2O$, The ion source 5 was supplied from the gas inlet 6 with the gestalt the mixed gas shown in the following table 3, or benzene independent (comparative example 2), using triethylaluminum $(C_2H_5)_3$aluminum as an organic compound containing aluminum. In Example 4, as introductory gas, namely, benzene, hetero methyl disiloxane, In Example 6, benzene was used [Example 5] as introductory gas by the comparative example 2 using the mixed gas of oxygen, using the mixed gas of benzene and triethylaluminum as introductory gas, using the mixed gas of benzene and a tetramethylsilane as introductory gas. It mixed by the setting-up flow rate shown in the following table 3 with the flow control device which is not illustrated, and each gas controlled the flow, and supplied it from the gas introducing pipe 17.

[0058]

[Table 3]

[0059]Subsequently, in the part distant from the central part in the vacuum housing 11 100 mm, the absorbable magnetic field (875 gauss) was efficiently formed for microwave by sending the current of 300A through the magnet coils 20a and 20b. Plasma was generated by introducing the microwave (frequency of 2.45 GHz) of the output of the microwave power supplies 19-1000W into the vacuum housing 11 via the waveguide 18 in this state. Simultaneously with the plasma generation, the hard carbon film 21 was formed by making voltage-2kV and duty (duty) ratio 1% of pulse voltage impress to the substrate 12 from the bias power supply 15 via the high insulation feed through 14.

[0060]About the carbon film obtained by Examples 4-6 and the comparative example 2, it investigated by Raman-spectrum analysis. As a result, any carbon film showed the large peak near 1500-1600-cm^{-1}, and has checked that it was a hard carbon film of amorphous structure.

[0061]About the carbon film obtained by Examples 4-6 and the comparative example 2, X linear-light electronic spectroscopic analysis analyzed elementary composition, and

Vickers hardness was measured. The coefficient of friction of said carbon film was counted with the ball one disk type frictional testing machine. As conditions for a rubbing test, 2N and speed were carried out in 0.1 m /, and atmosphere was a stainless steel (JIS:SUS304) ball and load the temperature of 30 **, and 400 ** for the mating material sec. The result is shown in the following table 4.

[0062]

[Table 4]

[0063]The hard carbon film of Examples 4 and 5 which have the amorphous structure containing silicon so that clearly from the result of said table 4, And it turns out that the hard carbon film of Example 6 which has the amorphous structure containing aluminum shows the low coefficient of friction of a single or less figure by the rubbing test in the atmosphere with a temperature of 30 ** compared with the hard carbon film of the comparative example 2. Especially the point that should be noted is a point which shows the coefficient of friction with a low hard carbon film of Examples 4-6 also in the rubbing test in the atmosphere with a temperature of 400 **. It damages at this temperature and the hard carbon film of the comparative example 2 shows a high friction coefficient. This shows that heat resistance of the hard carbon film of Examples 4-6 is improving substantially.

[0064]The organic compound gas which contains chromium in Examples 4-6 mentioned above as an organic compound containing a semiconductor or metal (for example, bis(cyclopentadienyl) clo NIUMU; $(C_5H_5)_2Cr$), The organic compound gas containing titanium (for example, cyclopentadienyl cyclo OKUTATETORAENII titanium; $(C_5H_5)(C_8H_8)Ti$), The organic compound gas which contains chromium as an organic compound containing a semiconductor or metal, and oxygen (for example, tris (acetylacetonate) clo NIUMU; $(C_5H_7O_2)_3Cr$), Even if it used the organic compound gas

(for example, tetraethoxy titanium; $(OC_2H_5)_4Ti$) containing titanium, the hard carbon film which has performance equivalent to Examples 4-6 was able to manufacture.

[0065]

[Effect of the Invention]As explained in full detail above, according to this invention, it excels in the friction characteristic in the inside of the atmosphere, and heat resistance, and a hard carbon film which can raise an industrial machine, a car, and the performance and the life of parts of an aerospace instrument, and a manufacturing method for the same can be provided.

[Translation done.]